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PHOTOCHEMISTRY OF IRON AND RUTHENIUM CARBONYL
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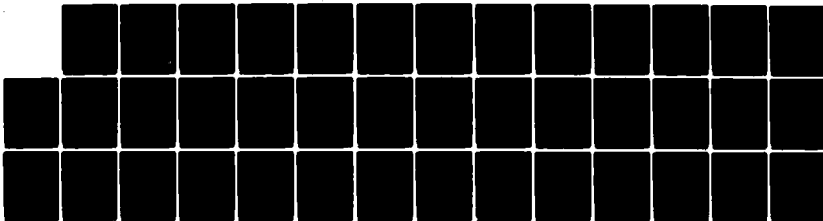
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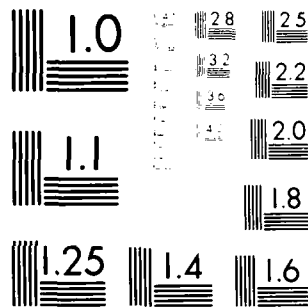
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The near-UV photochemistry of $M(CO)_4PPh_3$ and $HM(SiEt_3)(CO)_3(PPh_3)$ ($M = Fe, Ru$) has been investigated. The $HM(SiEt_3)(CO)_3(PPh_3)$ complexes have a meridional structure with the $-H$ cis to both PPh_3 and the $-SiEt_3$ and are referred to as the cis-mer isomer. In low temperature (~ 100 K) rigid organic glasses the $M(CO)_4PPh_3$ undergoes dissociative loss of CO to form the sixteen-electron $M(CO)_3PPh_3$, $M(CO)_3(PPh_3)(2-MeTHF)$, $M(CO)_3(PPh_3)(1-C_5H_{10})$, or cis-mer and fac- $HM(SiEt_3)(CO)_3(PPh_3)$ complex when the organic glass is an alkane, 2-MeTHF, 1-C₅H₁₀, or Et₃SiH, respectively. The fac- $HM(SiEt_3)(CO)_3(PPh_3)$ complexes undergo thermal isomerization to the cis-mer isomer upon warmup to 298 K. Near-UV excitation of cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$ at ~ 100 K in an organic glass gives evidence for both the loss of CO and reductive elimination of Et₃SiH. Photochemistry of the complexes at 298 K in fluid solution accords well with photoreactions observed at ~ 100 K in rigid media. Irradiation of cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$ in a hydrocarbon solution of Ph₃SiH at 298 K results in the formation of cis-mer- $HM(CO)_3(SiPh_3)(PPh_3)$ and Et₃SiH with a 313 nm quantum yield of ~ 0.6 . The process is photochemically reversed if the cis-mer- $HM(SiPh_3)(CO)_3(PPh_3)$ is irradiated in the presence of excess Et₃SiH. Irradiation of cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$ in a hydrocarbon solution at 298 K in the presence of ¹³CO yields both ¹³CO-enriched $M(CO)_4PPh_3$ and ¹³CO-enriched cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$. Irradiation of cis-mer- $HM(SiR_3)(CO)_3(PPh_3)$ ($R = OMe, OEt$) or cis-mer- $HRu(SiMeCl_2)(CO)_3(PPh_3)$ at 298 K in the presence of Et₃SiH yields cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$, establishing the light-induced reductive elimination of R_3SiH to occur for a wide range of R groups for these complexes.

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"PHOTOCHEMISTRY OF IRON AND RUTHENIUM CARBONYL COMPLEXES: EVIDENCE FOR
LIGHT-INDUCED LOSS OF CARBON MONOXIDE AND REDUCTIVE ELIMINATION OF
TRIETHYLSILANE FROM cis-mer-HM(SiEt₃)(CO)₃(PPh₃)"

by

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Photochemistry of Iron and Ruthenium Carbonyl Complexes: Evidence for
Light-Induced Loss of Carbon Monoxide and Reductive Elimination of
Triethylsilane from *cis-mer*-HM(SiEt₃)(CO)₃(PPh₃)

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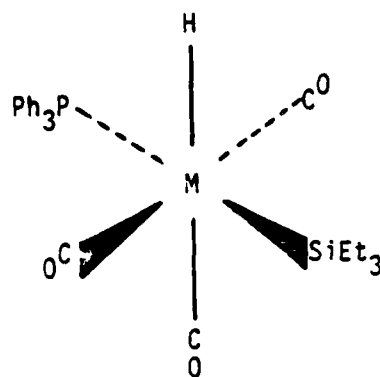
Abstract

The near-UV photochemistry of $M(CO)_4PPh_3$ and $HM(SiEt_3)(CO)_3(PPh_3)$ ($M = Fe, Ru$) has been investigated. The $HM(SiEt_3)(CO)_3(PPh_3)$ complexes have a meridional structure with the -H cis to both PPh_3 and the $-SiEt_3$ and are referred to as the cis-mer isomer. In low temperature (~ 100 K) rigid organic glasses the $M(CO)_4PPh_3$ undergoes dissociative loss of CO to form the sixteen-electron $M(CO)_3PPh_3$, $M(CO)_3(PPh_3)(2-MeTHF)$, $M(CO)_3(PPh_3)(1-C_5H_{10})$, or cis-mer and fac- $HM(SiEt_3)(CO)_3(PPh_3)$ complex when the organic glass is an alkane, 2-MeTHF, 1-C₅H₁₀, or Et₃SiH, respectively. The fac- $HM(SiEt_3)(CO)_3(PPh_3)$ complexes undergo thermal isomerization to the cis-mer isomer upon warmup to 298 K. Near-UV excitation of cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$ at ~ 100 K in an organic glass gives evidence for both the loss of CO and reductive elimination of Et₃SiH. Photochemistry of the complexes at 298 K in fluid solution accords well with photoreactions observed at ~ 100 K in rigid media. Irradiation of cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$ in a hydrocarbon solution of Ph_3SiH at 298 K results in the formation of cis-mer- $HM(CO)_3(SiPh_3)(PPh_3)$ and Et₃SiH with a 313 nm quantum yield of ~ 0.6 . The process is photochemically reversed if the cis-mer- $HM(SiPh_3)(CO)_3(PPh_3)$ is irradiated in the presence of excess Et₃SiH. Irradiation of cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$ in a hydrocarbon solution at 298 K in the presence of ¹³CO yields both ¹³CO-enriched $M(CO)_4PPh_3$ and ¹³CO-enriched cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$. Irradiation of cis-mer- $HM(SiR_3)(CO)_3(PPh_3)$ ($R = OMe, OEt$) or cis-mer- $HRu(SiMeCl_2)(CO)_3(PPh_3)$ at 298 K in the presence of Et₃SiH yields cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$, establishing the light-induced reductive elimination of R₃SiH to occur for a wide range of R groups for these complexes.

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Photoexcitation of organometallic molecules can yield reactive fragments via excited state chemistry involving dissociative processes including extrusion of two-electron donor ligands, metal-metal bond cleavage, and reductive elimination of small molecules such as H_2 from a cis-dihydride.¹ Information concerning the relative importance of such excited state processes is necessary to develop catalytic applications of organometallic photochemistry. In this article we wish to report on the low temperature (~ 100 K) photochemistry of $M(CO)_4PPh_3$ and cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$ ($M = Fe, Ru$), 1a and 1b. The new finding is that reductive elimination of a silicon-hydride can be a quantum efficient process that can occur competitively with loss of two-electron donor ligands even in low temperature organic glasses. The reductive elimination of H_2 from cis-dihydride is a well-known photoreaction,² but reductive elimination of a bulky molecule such as Et_3SiH is somewhat surprising in view of the large cage effect expected for a rigid organic glass. The photochemistry of the systems represented here is of importance in understanding the photocatalyzed hydrosilylation of alkenes that can be effected by the irradiation of $M(CO)_4PPh_3$ in the presence of R_3SiH /alkene mixtures.³



- 1
a, $M = Fe$
b, $M = Ru$

Experimental

Instruments. UV-VIS absorption spectra were recorded on a Cary 17 or Hewlett-Packard 8451A diode array spectrophotometer. IR absorption spectra were recorded with a Perkin-Elmer 180 grating or Nicolet 7199 Fourier transform spectrometer. Low-temperature IR spectra were obtained by using a Precision Cell, Inc. Model P/N 21,000 variable-temperature cell with NaCl outer windows, using liquid N₂ as coolant. Care was taken to ensure that low-temperature IR results were unaffected by the source of the spectrometer. This was established by showing that spectra of intermediates could be reproduced after prolonged exposure to the interrogating beam of the spectrometer. NMR spectra were recorded with a JEOL FX90Q Fourier transform or Bruker 250 or 270 MHz Fourier transform spectrometer.

Irradiations. Photochemical reactions were carried out using a Bausch and Lomb SP200 200-W high pressure Hg lamp with a Pyrex® water filter or a Hanovia 550-W medium pressure Hg lamp unless otherwise noted. Quantum yields at 313 nm were measured in a merry-go-round⁴ using $\sim 10^{-3}$ M cis-mer-HM(SiR₃)(CO)₃(PPh₃) (M = Fe, R = Ph; M = Ru, R = Et) with appropriate ligand concentrations. 3.0 mL samples in 13 x 100 nm test tubes were freeze-pump-thaw degassed prior to irradiation. The light source was a 500-W Hanovia medium pressure Hg lamp equipped with a chemical (K₂CO₃/K₂CrO₄ solution) and glass (Corning #7-54) filter system to isolate the 313 nm Hg emission. Ferrioxalate actinometry⁵ was used to determine light intensity, which was typically $\sim 10^{-8}$ einstein/min.

Materials. All manipulations of air-sensitive materials were carried out in a N₂-filled Vacuum Atmospheres He-63-P Dri-Lab glovebox with an attached He-493 Dri-Train or under Ar using conventional Schlenk techniques. Methylcyclohexane

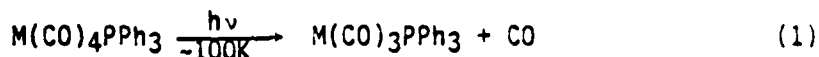
(99%, Aldrich), 3-methylpentane (99%, Aldrich) and 1-pentene (99%, Phillips) were passed through grade 1 alumina (neutral, Woelm) and degassed prior to use. 2-Methyltetrahydrofuran (Aldrich) was freshly distilled from Na under N_2 . Triphenylphosphine (Aldrich) was recrystallized three times from absolute EtOH prior to use. $Fe(CO)_5$ and $Ru_3(CO)_{12}$ were obtained from Strem Chemicals and used as received. Triethylsilane was obtained from Petrarch and used without further purification. Triphenylsilane (Aldrich) was recrystallized from hexane before use. Et_3SiD was prepared using procedures previously described.⁶ ^{13}CO (90% ^{13}C) was obtained from Cambridge Isotope Laboratories.

Literature procedures⁷ were used to synthesize $M(CO)_4PPh_3$ ($M = Fe, Ru$). The cis-mer- $HM(SiR_3)(CO)_3PPh_3$ ($M = Fe, Ru$; $R = Et, Ph$) complexes were prepared by the irradiation of an alkane or toluene solution of $M(CO)_4PPh_3$ containing excess $HSiR_3$ under Ar at 298 K. Removal of excess R_3SiH and solvent left a brownish-yellow oil for $M = Fe$; $R = Et$ and a greenish-yellow solid for $M = Fe$; $R = Ph$. In the case of $M = Ru$, an orange solid was isolated for both $R = Et$ and Ph which could then be purified by recrystallization from hexane. The compound cis- $HFe(SiEt_3)(CO)_4$ was reacted with PPh_3 in hexane as reported by Cardaci⁸ to give a second isomer of $HFe(SiEt_3)(CO)_3(PPh_3)$, a meridional isomer where the $-H$ is trans to the PPh_3 . UV-VIS, IR, and 1H - and ^{13}C -NMR spectroscopies were used to characterize these compounds and the results are listed in Tables I and II. The cis-mer- $HM(SiR_3)(CO)_3(PPh_3)$ ($M = Fe, Ru$; $R = OMe, OEt$) and cis-mer- $HRu(SiMeCl_2)(CO)_3(PPh_3)$ complexes were prepared by irradiating $M(CO)_4PPh_3$ in the presence of the R_3SiH or $MeCl_2SiH$ in alkane solvent followed by removal of solvent and excess silane under vacuum. Samples were then taken up in alkane-containing Et_3SiH to study the light-induced conversion to cis-mer- $HM(SiEt_3)(CO)_3(PPh_3)$.

Results and Discussion

Photochemistry of $M(CO)_4PPh_3$. Previous studies^{9,10} of $M(CO)_4(P\text{-donor})$ ($M = Fe, Ru$) have led to the conclusion that CO loss, not P-donor loss, dominates the excited state chemistry of $M(CO)_4(P\text{-donor})$. In the present work we have examined the IR spectral changes accompanying near-UV irradiation of $M(CO)_4PPh_3$ in various organic glasses at -100 K to monitor the loss of CO and to determine the nature of the photoproduct when the glass is, or contains, a two-electron donor or an oxidative addition substrate, Figures 1-3 and Tables I and II.

All data are consistent with loss of CO upon photoexcitation of $M(CO)_4PPh_3$. In alkane media the metal-containing product is a sixteen-electron species as indicated in equation (1).^{10b} Initially, <15% conversion, the loss of one CO



($\pm 15\%$) per $M(CO)_4PPh_3$ consumed is established by a quantitative comparison of the growth of the 2132 cm^{-1} absorption assigned to the free CO and the decline of absorptions due to $M(CO)_4PPh_3$.¹¹ In no case do we observe loss of PPh_3 , since IR spectral features for the $M(CO)_4$ ¹² that would accompany PPh_3 loss are not observed.

The lack of a strong interaction of the $M(CO)_3PPh_3$ fragments with the alkane glasses is deduced from the relatively low energy IR absorptions in the CO stretching region compared to $M(CO)_4PPh_3$ or $HM(CO)_3(SiEt_3)(PPh_3)$, Table I. It is also noteworthy that $Ru(CO)_3PPh_3$ shows significantly lower energy UV-VIS absorption maxima than $Ru(CO)_4PPh_3$, consistent with the expected stabilization of the LUMO upon converting $Ru(CO)_4PPh_3$ to $Ru(CO)_3PPh_3$.^{10b} The two band IR spectrum for $Ru(CO)_3PPh_3$, Figure 1, signals a C_{3v} geometry whereas $Fe(CO)_3PPh_3$, Figure 2, appears to have a C_s symmetry, since a three-band spectrum is found in the CO stretching region. Similar differences in the geometry of other sixteen-electron

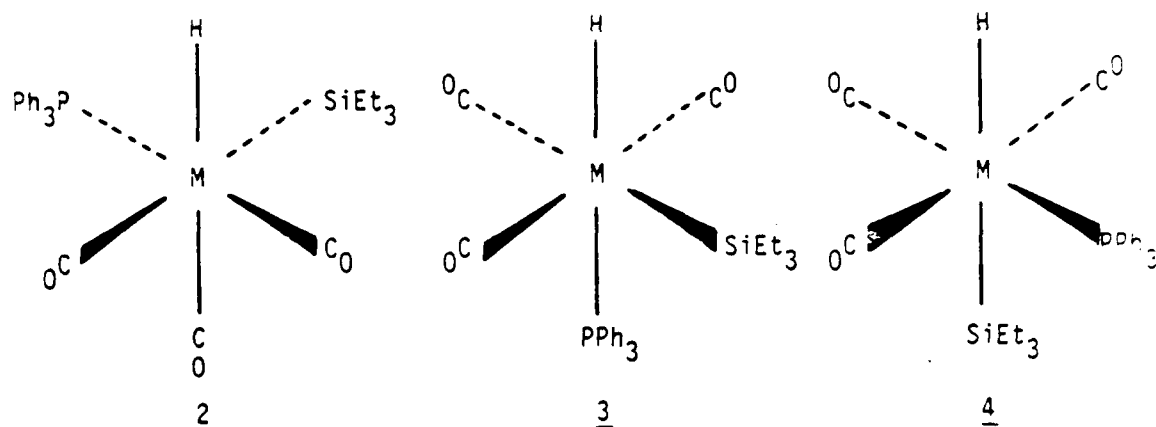
$M(CO)_3L$ fragments have been observed.¹³ Warmup of $M(CO)_3PPh_3$ in the absence of added ligands yields regeneration of $M(CO)_4PPh_3$. However, warmup of a ~ 100 K alkane glass containing photogenerated $M(CO)_3PPh_3$ and PPh_3 yields $M(CO)_3(PPh_3)_2$ consistent with the unsaturated nature of the $M(CO)_3PPh_3$.

In a 2-MeTHF or 1-C₅H₁₀ glass irradiation of $M(CO)_4PPh_3$ yields $M(CO)_3-(PPh_3)(2-MeTHF)$ or $M(CO)_3(PPh_3)(1-C_5H_{10})$, respectively, as evidenced by the very different IR spectral changes compared to those in the alkane glasses. For $M = Fe$ or Ru , the differences in the IR spectral changes accompanying irradiation in an alkane compared to 1-C₅H₁₀ are shown in Figures 1 and 2. The similarity of the pattern of absorption in the CO stretching region for the Fe and Ru complexes indicates similar structures. The 2-MeTHF is a sterically encumbered, σ -donor only ligand that should form a substitution labile complex. The significantly lower energy IR absorptions for the photoproduct in 2-MeTHF compared to the photoproduct in the alkene glass is consistent with the fact that 2-MeTHF is not a π -bonding ligand. The $M(CO)_4PPh_3$ complexes do show slightly lower energy (~ 60 cm⁻¹) absorptions in 2-MeTHF than in the alkane solvent, but the ~ 30 cm⁻¹ lower energy absorptions for $M(CO)_3(PPh_3)(2-MeTHF)$ in 2-MeTHF compared to $M(CO)_3PPh_3$ in an alkane is too great a difference to attribute to a solvent effect on the spectrum of the $M(CO)_3PPh_3$. Though the oxygen-donor 2-MeTHF is a weakly bound ligand it is probably best viewed as such toward the $M(CO)_3PPh_3$ fragment, and the species in 2-MeTHF should not be regarded as 16 e⁻ complexes. The $M(CO)_3(PPh_3)(L)$ ($L = 2-MeTHF, 1-C_5H_{10}$) complexes, and most especially the Fe complexes, undergo very rapid secondary photoreaction to yield $M(CO)_2(PPh_3)_2L_2$ as evidenced by the appearance of additional CO absorption (2132 cm⁻¹) and new metal carbonyl absorptions.

Irradiation of $M(CO)_4PPh_3$ in a low temperature (~ 100 K) Et₃SiH matrix or an alkane matrix containing Et₃SiH results in reaction to form what appears to be

one stable and one unstable isomer of $\text{HM}(\text{CO})_3(\text{SiEt}_3)(\text{PPh}_3)$, Figures 1-3. The fact that one of the products is unstable is established by warming the sample to 298 K. For both the Fe and Ru systems the warming of the photoproduct mixture to 298 K results in IR spectral changes revealing the formation of more of the stable product at the expense of the unstable product. The stable product is the same product that results upon irradiating $\text{M}(\text{CO})_4\text{PPh}_3$ at 298 K in the presence of Et_3SiH . Cooling the 298 K product to at least 100 K in the dark does not regenerate the low temperature photoproduct. The IR spectral changes that occur upon irradiation of $\text{M}(\text{CO})_4\text{PPh}_3$ at ~100 K in Et_3SiH are very different from those in an alkane matrix establishing that the $\text{M}(\text{CO})_3\text{PPh}_3$ does react with Et_3SiH at low temperature. As shown in Figure 3, the use of a small amount of Et_3SiH (~10% by volume) in an alkane matrix allows detection of both $\text{Ru}(\text{CO})_3\text{PPh}_3$ and two isomers of $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. Warmup results in loss of $\text{Ru}(\text{CO})_3\text{PPh}_3$ and growth of additional $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. Photolysis of $\text{Ru}(\text{CO})_4\text{PPh}_3$ in an alkane/ Et_3SiH (1/1) matrix yields only $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$, Figure 1. A recent report on the oxidative addition of Et_3SiH to photogenerated $\text{Et}_3\text{SiCo}(\text{CO})_3$ at low temperature¹⁴ and low temperature oxidative addition of H_2 ¹⁵ to $\text{Fe}(\text{CO})_4$ or to $\text{HCo}(\text{CO})_3$ provide precedent for the 100 K oxidative addition chemistry reported here. Interestingly, we have found that lowering the temperature by ~5 K in the case of $\text{Fe}(\text{CO})_4\text{PPh}_3$ shows that $\text{Fe}(\text{CO})_3\text{PPh}_3$ can be formed in neat Et_3SiH ; warmup yields $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. A study to detail the thermal parameters for addition of Et_3SiH to $\text{Fe}(\text{CO})_3\text{PPh}_3$ is underway in this laboratory.

There are several possible structures for the $\text{HM}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ complexes as shown in 1-4. Structure 3 was recently assigned to the thermal product from reaction of PPh_3 with cis- $\text{HFe}(\text{SiPh}_3)(\text{CO})_4$.⁸ The IR bands in the CO region were found⁸ to be at 2065(s), 2000(s), 1975(sh) cm^{-1} in hexane with a hydride signal in

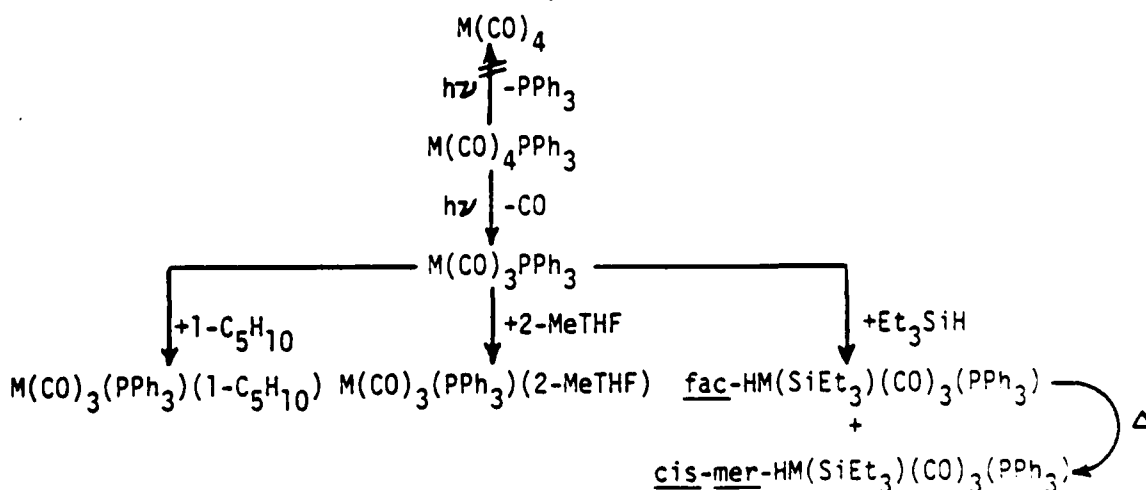


the ^1H -NMR showing a $^2J_{\text{P-H}}$ coupling of 47 Hz in Et_2O . Our data for the photo-product from irradiation of $\text{Fe}(\text{CO})_4\text{PPh}_3$ in the presence of Ph_3SiH is very different, Tables I and II, and at least shows that the structure of $\text{HFe}(\text{SiPh}_3)(\text{CO})_3(\text{PPh}_3)$ formed photochemically is not that reported in reference 8. We have found the IR bands at 2061 and 1999 cm^{-1} in alkane when cis- $\text{HFe}(\text{SiPh}_3)(\text{CO})_4$ is reacted thermally with PPh_3 at -20°C in accord with data in reference 8. The IR spectra and $^2J_{\text{P-H}}$ coupling constants for $\text{HFe}(\text{SiPh}_3)(\text{CO})_3(\text{PPh}_3)$ and $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ formed photochemically at 298 K are quite similar, and the values of $^2J_{\text{P-H}}$ for all $\text{HM}(\text{SiR}_3)(\text{CO})_3(\text{PPh}_3)$ complexes at 298 K are most consistent with a cis disposition of the PPh_3 and the $-\text{H}$.¹⁶ The IR spectra in the CO region for the $\text{HM}(\text{SiR}_3)(\text{CO})_3(\text{PPh}_3)$ complexes at 298 K are very similar to those for $\text{HRu}(\text{SiR}_3)(\text{CO})_3(\text{PPh}_3)$ complexes characterized previously¹⁷ as having structure 1. We thus adopt structure 1 for $\text{HM}(\text{SiR}_3)(\text{CO})_3(\text{PPh}_3)$ complexes formed via irradiation of $\text{M}(\text{CO})_4\text{PPh}_3$ in the presence of R_3SiH at 298 K.

The other low temperature photoproduct $\text{HM}(\text{SiR}_3)(\text{CO})_3(\text{PPh}_3)$ is assigned structure 2. The IR data are inconsistent with structure 1¹⁷ or 3,⁸ and we rule

out 4, since the -H and -SiR₃ would most likely be cis to each other upon oxidative addition in a rigid matrix. This leaves the facial isomer 2 as the other low temperature photoproduct. The two-band IR pattern in the CO region at low temperature is consistent with the facial arrangement. To summarize, Scheme I illustrates the photochemistry of M(CO)₄PPh₃; all photoproducts arise from the loss of CO, not PPh₃. The quantum yield for loss of CO has been determined to exceed 10⁻¹ at 298 K.^{9,10}

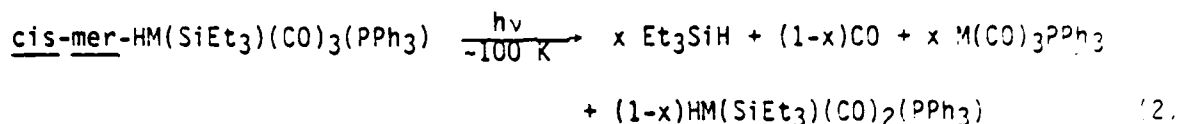
Low Temperature Photochemistry of 1a and 1b. The consequences of near-UV irradiation of 1 have been investigated over a wide temperature range and in a variety of media. The conclusion is that loss of CO and R₃SiH are competitive processes from the lowest excited state. The low temperature experiments supporting this conclusion will now be detailed.



Scheme I. Photochemistry of M(CO)₄PPh₃ (M = Fe, Ru).

Spectral changes accompanying irradiation of 1 at 100 K provide direct evidence that light-induced loss of CO and Et₃SiH do occur, Figures 4 and 5. Two key absorptions grow as the starting material is consumed. The feature at 2132

cm^{-1} is characteristic of uncomplexed CO and the broader band at 2104 cm^{-1} is associated with the Si-H stretch of Et_3SiH . The uncomplexed CO and the Et_3SiH appear as photoproducts when the matrix is alkane, 1- C_5H_{10} , or 2-MeTHF. Both CO and Et_3SiH are detected at the lowest extent conversions measurable and their ratio is constant at the initial stages (<15% conversion) of the reaction. Interestingly, the Ru complex appears to undergo photoisomerization from structure 1 to 2 at 100 K in an alkane matrix, Figure 5. However, irradiation of the Ru complex in the 1- C_5H_{10} (or 2-MeTHF, not shown) matrix suppresses the isomerization and there appears to be more free Et_3SiH relative to CO. These results suggest that the photoisomerization proceeds via loss of Et_3SiH from 1b followed by back reaction to give the same product derived from light-induced CO loss from $\text{Ru}(\text{CO})_4\text{PPh}_3$ at low temperature. The donor matrix molecules, 1- C_5H_{10} or 2-MeTHF, presumably can saturate the $\text{Ru}(\text{CO})_3\text{PPh}_3$ prior to reaction with the Et_3SiH to give the facial isomer of $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. The Fe complex does not show detectable isomerization in an alkane matrix, but irradiation in the presence of Et_3SiH at low temperature does yield the isomer of structure 2, Figure 4. There are clearly some subtle differences in the photochemistry of 1a and 1b, but establishing the reasons will be difficult. The species $\text{Ru}(\text{CO})_3\text{PPh}_3$ and $\text{Fe}(\text{CO})_3\text{PPh}_3$ have different structures and the orientation of the 16 e^- fragment relative to the extruded Et_3SiH may be different as well. An important quantitative conclusion can be made from the appearance of Et_3SiH and CO upon photolysis of 1. When isomerization of 1 to 2 is unimportant, the appearance of CO and Et_3SiH accounts for all of the 1 consumed in the photoreaction, within an experimental error of $\pm 20\%$. This means that other possible primary photoreactions are relatively unimportant. Thus, homolysis of M-H, M-SiEt₃, and loss of PPh₃ are ruled out as important photoprocesses. Equation (2) appears to represent the photochemistry of 1 at -100 K.



$$\text{M} = \text{Fe}, x = 0.60 \pm 0.12$$

$$\text{M} = \text{Ru}, x = 0.60 \pm 0.12$$

The light-induced appearance of Et_3SiH from 1 at low temperature is accompanied by the appearance of the metal carbonyl product expected assuming that the resulting $\text{M}(\text{CO})_3\text{PPh}_3$ has the same structure as produced upon irradiation of $\text{M}(\text{CO})_4\text{PPh}_3$. In an alkane $\text{M}(\text{CO})_3\text{PPh}_3$ is produced; in 1- C_5H_{10} $\text{M}(\text{CO})_3(\text{PPh}_3)$ - (1- C_5H_{10}) is produced; and in 2-MeTHF $\text{M}(\text{CO})_3(\text{PPh}_3)(2\text{-MeTHF})$ is formed. The formation of structure 2 upon irradiation in the presence of Et_3SiH also accords well with the formation of $\text{M}(\text{CO})_3\text{PPh}_3$ via loss of Et_3SiH from photoexcited 1.

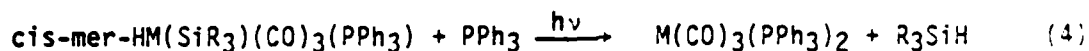
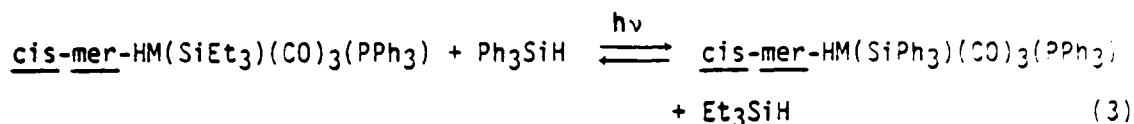
Identification of the metal-containing product from loss of Et_3SiH from 1 in the various media is possible because all of the products can be made independently by irradiation of $\text{M}(\text{CO})_4\text{PPh}_3$. The loss of CO from 1 should yield $\text{HM}(\text{SiEt}_3)(\text{CO})_2(\text{PPh}_3)$ in unreactive matrices or $\text{HM}(\text{SiEt}_3)(\text{CO})_2(\text{PPh}_3)(\text{L})$ in donor (L) matrices. The IR spectral changes do show product absorptions that are not attributable to fac- $\text{HM}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ or to the $\text{M}(\text{CO})_3\text{PPh}_3$ or $\text{M}(\text{CO})_3(\text{PPh}_3)(\text{L})$ from the loss of Et_3SiH . For example, in Figure 4 the features that grow in at 1924 and 1895 cm^{-1} for the irradiation of 1a in the $\text{Et}_3\text{SiH}/3\text{-methylpentane}$ glass could be attributed to $\text{HFe}(\text{SiEt}_3)(\text{CO})_2(\text{PPh}_3)$. The same features might, in fact, be present in the pure 3-methylpentane matrix, but strong features at 1921 and 1886 cm^{-1} due to $\text{Fe}(\text{CO})_3\text{PPh}_3$, Figure 2, obscure the region. The 1921 cm^{-1} feature does show a shoulder on the high energy side and the absorbance at 1921 cm^{-1} relative to the absorbance for the 2003 cm^{-1} band of $\text{Fe}(\text{CO})_3\text{PPh}_3$ is higher than for $\text{Fe}(\text{CO})_3\text{PPh}_3$ generated from $\text{Fe}(\text{CO})_4\text{PPh}_3$. Thus, it is logical to assume that the Fe-containing product from CO loss from 1a absorbs at ~1920 cm^{-1} . The

lack of higher energy absorptions for the CO loss product from 1a in Et₃SiH vs. an alkane matrix suggests that the Et₃SiH does not oxidatively add to the coordinatively unsaturated metal.

The IR spectral changes accompanying the irradiation of 1b at 100 K also show product features in the CO stretching region that can be attributed to the Ru-containing products derived from CO loss. For example, in Figure 5, the prominent band at 1947 cm⁻¹ and that at ~1985 cm⁻¹ in the alkane matrix are not due to Ru(CO)₃PPh₃, Figure 1, and are logically associated with the HRu(SiEt₃)(CO)₂(PPh₃) species. In the 1-C₅H₁₀ matrix the 1947 cm⁻¹ feature is absent, consistent with chemistry resulting from interaction with the sixteen-electron HRu(SiEt₃)(CO)₂(PPh₃) and the donor matrix. However, the nature of the product may not be merely a 1-C₅H₁₀ complex, since there is the possibility of chemistry associated with the interaction of the sixteen-electron hydride species with the olefin. This issue requires further study. Irradiation of 1b in a Et₃SiH matrix yields the fac-HRu(SiEt₃)(CO)₃(PPh₃). There are features in the metal carbonyl region of the IR that indicate that at least one other product is formed, consistent with CO loss from 1b. However, the prominent band at 1947 cm⁻¹ in the alkane matrix is not present indicating that the Et₃SiH may oxidatively add to the photogenerated HRu(SiEt₃)(CO)₂(PPh₃).

Photochemistry of 1 at 298 K in Fluid Solution. The photochemistry of 1 in 298 K solution accords well with findings from the irradiation of 1 in organic glasses at ~100 K. Irradiation of 1 has been carried out in the presence of various species in solution to establish the importance of reductive elimination of R₃SiH in fluid solution.

Figure 6 shows results relating to the photochemistry represented by equations (3) and (4). As the IR and ¹H-NMR spectral changes show, the

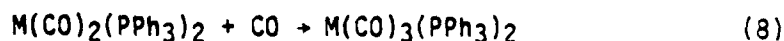
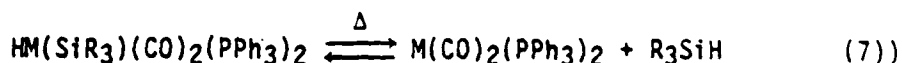
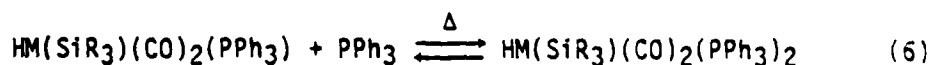
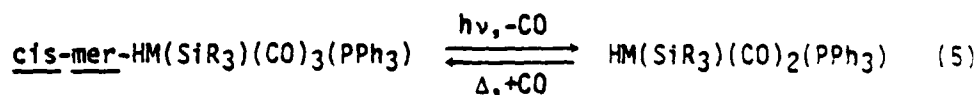


irradiation of 1 in the presence of Ph_3SiH results in the exchange process given in equation (3). The photochemical exchange process can be effected essentially quantitatively either starting with 1 or with the $-\text{SiPh}_3$ analogue in the presence of excess Ph_3SiH or Et_3SiH , respectively. Typical photoreaction conditions were 1-5 mM of the metal complexes irradiated with near-UV excitation in hydrocarbon (alkane or C_6D_6) solution containing 10-50 mM of R_3SiH . The $^1\text{H-NMR}$ in the hydride region establishes that total hydride concentration is conserved in the photoreaction, and IR spectral changes, especially those in the Si-H stretching region, are also consistent with quantitative exchange processes. The irradiation of 1 or the $-\text{SiPh}_3$ analogues under the same conditions except in the presence of 10-50 mM PPh_3 instead of R_3SiH results in clean conversion to $\text{M}(\text{CO})_3(\text{PPh}_3)_2$. The reactions represented by equations (3) and (4) occur with a 313 nm quantum yield of 0.6 ± 0.1 for both the Fe and Ru species. Thus, the chemistry is not only clean but occurs with high quantum efficiency. Though the reactions have not been studied in detail, we note that $\text{cis-mer-HM}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ is the photoproduct from near-UV irradiation of $\text{cis-mer-HM}(\text{SiR}_3)(\text{CO})_3(\text{PPh}_3)$ ($\text{M} = \text{Fe, Ru}$; $\text{R} = \text{CMe, OEt}$) or $\text{cis-mer-HRu}(\text{SiMeCl}_2)(\text{CO})_3(\text{PPh}_3)$ in 298 K alkane solutions. These examples lend credence to the conclusion that light-induced reductive elimination of R_3SiH could be important for a wide range of R.

The photochemistry represented by both equations (3) and (4) is consistent with clean and quantum efficient reductive elimination of R_3SiH from 1 and the $\text{Ph}_3\text{Si-}$ analogues in fluid solution. These data do not reveal whether there is any

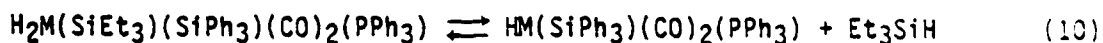
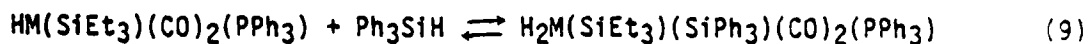
role for loss of CO from 1 in fluid solution. However, several experiments have been done that do show that CO loss is a process that competes with reductive elimination of R₃SiH from photoexcited 1. Direct evidence for loss of CO from 1 comes from the initial product distribution from irradiation of 1b in the presence of ¹³CO in toluene solution. Both ¹³CO-enriched Ru(CO)₄PPh₃ and ¹³CO-enriched 1c are formed as products at ~10% conversion as evidenced by ¹³C-NMR. Irradiation of cis-mer-HFe(SiPh₃)(CO)₃(PPh₃) under the same conditions gives ¹³CO-enriched Fe(CO)₄PPh₃ and cis-mer-HFe(SiPh₃)(CO)₃(PPh₃), but the lowest extent conversion where the ¹³C-NMR could be recorded was ~30%. The data indicate that CO loss is competitive with R₃SiH loss, but the relative importance could not be measured by ¹³C-NMR due to low signal-to-noise at low extent conversions. However, the ¹³CO exchange results do accord well with the low temperature photolysis of 1 where CO is detected directly by IR.

A puzzling finding in view of the ¹³CO exchange results is that the photolysis of 1 in the presence of PPh₃ does not yield any detectable products other than M(CO)₃(PPh₃)₂. It is possible that the CO substitution product, HM(SiR₃)(CO)₂(PPh₃)₂ is very labile with respect to thermal elimination of Et₃SiH, owing to steric crowding. Thus, primary loss of CO from 1 would be a route to M(CO)₃(PPh₃)₂ via the sequence represented by equations (5)-(8). Of course, M(CO)₃(PPh₃)₂

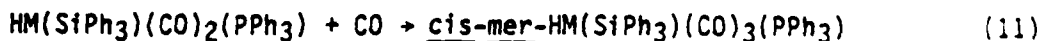


formation occurs, at least in part, via prompt reductive elimination of R_3SiH from 1 to form $M(CO)_3PPh_3$ that can be scavenged by PPh_3 . It is possible that $HM(SiEt_3)(CO)_2(PPh_3)_2$ does not occur because PPh_3 is incapable of capturing $HM(SiEt_3)(CO)_2(PPh_3)$, equation (6), in competition with back reaction with the photoejected CO. Irradiation of 1b in the presence of a less sterically demanding P-donor, $P(OCH_2)_3CEt$, yields $Ru(CO)_3(PPh_3)(P(OCH_2)_3CEt)$ and apparently substitution of a CO. A band is observed in the IR at $\sim 1974\text{ cm}^{-1}$ that we assign to $HRu(SiEt_3)(CO)_2(PPh_3)(P(OCH_2)_3CEt)$. The 1H -NMR in the hydride region shows new products when 1b is irradiated in the presence of $P(OCH_2)_3CEt$, but the spectrum is complicated suggesting several isomers and secondary photoproducts are formed. While the $P(OCH_2)_3CEt$ photosubstitution products have not been fully characterized, the irradiation at 1b in the presence of $P(OCH_2)_3CEt$ does at least confirm a role for CO loss from photoexcited 1b.

The light-induced incorporation of ^{13}CO into 1 and the CO photosubstitution by $P(OCH_2)_3CEt$ raises the issue of whether loss of CO from 1 can play a role in the R_3SiH exchange chemistry represented by equation (3). The point is that CO loss from 1 in the presence of Ph_3SiH could yield exchange via an oxidative addition/reductive elimination mechanism as indicated in equations (9) and (10)



followed by uptake of CO released in the primary step to complete the exchange chemistry, equation (11). We do find that irradiation of cis-mer- $HM(SiPh_3)-$



(CO)₃(PPh₃) in the presence of Et₃SiD does not give a quantitative yield of Ph₃SiH and the cis-mer-DM(SiEt₃)(CO)₃(PPh₃) that would be expected for exchange via a simple loss of Ph₃SiH followed by oxidative addition of Et₃SiD. Rather, the ²H- and ¹H-NMR data show formation of both Ph₃SiD and Ph₃SiH along with some Et₃SiH. The total amount of Ph₃SiH and Et₃SiH equals (±15%) the initial amount of cis-mer-HM(SiPh₃)(CO)₃(PPh₃). The M-containing products include both cis-mer-DM(SiEt₃)(CO)₃(PPh₃) and cis-mer-HM(SiEt₃)(CO)₃(PPh₃) as determined by ²H- and ¹H-NMR, respectively. No cis-mer-DM(SiPh₃)(CO)₃(PPh₃) could be detected in the ²H-NMR, presumably because there is an excess of Et₃SiD. In any event, the distribution of photoproducts in the presence of Et₃SiD demands a component of a mechanism other than one beginning with the light-induced loss of Ph₃SiH. The process represented by equations (9) and (10) could lead to the D/H scrambling, but other mechanisms for the scrambling are not easily ruled out with the available data. For example, concerted four-center exchange processes, binuclear, and free radical processes could also account for the observed results. However, we do not observe the irreproducibility in quantum yields often found for radical reactions and we have not detected products that could arise from binuclear reactions such as M-M bonded complexes. While it is difficult to rule out the four-center mechanisms, we favor the process represented by equations (9) and (10) because CO loss from 1 is a primary photoprocess. The conservation of protons in the hydride region of the ¹H-NMR during the light-induced R₃SiH exchange reactions rules out other reductive elimination processes (such as H₂ or disilane formation) from a species such as the dihydride in equations (9) and (10).

Reactivity of the Intermediate from Reductive Elimination of Et₃SiH from 1 Compared to Intermediate Formed from CO Loss from M(CO)₄PPh₃. Light-induced loss of CO from M(CO)₄PPh₃ occurs to yield the sixteen-electron species M(CO)₃PPh₃ that can be

scavenged by a two-electron donor such as $\text{P}(\text{OCH}_2)_3\text{CEt}$ or by an oxidative addition substrate such as R_3SiH . Likewise, reductive elimination of Et_3SiH from 1 yields, presumably, the same $\text{M}(\text{CO})_3\text{PPh}_3$. As a test of whether the $\text{M}(\text{CO})_3\text{PPh}_3$ from light-induced CO loss from $\text{M}(\text{CO})_4\text{PPh}_3$ has the same reactivity as from light-induced reductive elimination of R_3SiH from 1, we have irradiated samples of 1b or $\text{Ru}(\text{CO})_4\text{PPh}_3$ in hydrocarbon solutions of $\text{P}(\text{OCH}_2)_3\text{CEt}$ and Ph_3SiH and examined the initial ratio of $\text{Ru}(\text{CO})_3(\text{PPh}_3)(\text{P}(\text{OCH}_2)_3\text{CEt})$ and cis-mer- $\text{HRu}(\text{SiPh}_3)(\text{CO})_3(\text{PPh}_3)$ as a function of the ratio of $\text{P}(\text{OCH}_2)_3\text{CEt}$ and Ph_3SiH . The results are consistent with the conclusion that the reactivity is the same for the $\text{Ru}(\text{CO})_3\text{PPh}_3$ generated from irradiation of $\text{Ru}(\text{CO})_4\text{PPh}_3$ or 1b because the product ratio, Table III, is the same. The irradiation of 1b in the presence of $\text{P}(\text{OCH}_2)_3\text{CEt}$ does yield CO substitution, but this does not apparently affect the ratio of cis-mer- $\text{HRu}(\text{SiPh}_3)(\text{CO})_3(\text{PPh}_3)$ to $\text{Ru}(\text{CO})_3(\text{PPh}_3)(\text{P}(\text{OCH}_2)_3\text{CEt})$. When the reactivity of $\text{Ru}(\text{CO})_3\text{PPh}_3$ is investigated by irradiation of $\text{Ru}(\text{CO})_4\text{PPh}_3$ or 1b in the presence of Ph_3SiH and PPh_3 , the ratio of cis-mer- $\text{HRu}(\text{SiPh}_3)(\text{CO})_3(\text{PPh}_3)$ to $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ is different from $\text{Ru}(\text{CO})_4\text{PPh}_3$ and 1b at a given ratio of Ph_3SiH to PPh_3 . The photoproduct distribution from 1b is consistently richer in $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, consistent with CO loss from 1b providing an alternative route, possibly via equations (5)-(8), to the $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$.

Conclusions

→ Detailed studies of cis-mer- $\text{HM}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ ($\text{M} = \text{Ru}, \text{Fe}$) show that near-UV irradiation can result in reductive elimination of Et_3SiH as a primary photoprocess. Additionally, qualitative 298 K experiments show that Ph_3SiH , $(\text{MeO})_3\text{SiH}$, $(\text{EtO})_3\text{SiH}$, and MeCl_2SiH can be reductively eliminated from the appropriate cis-mer metal complex, establishing elimination of R_3SiH as a viable process for a wide range of R. From 298 K studies of cis-mer- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$, it appears that light-induced reductive elimination of R_3SiH yields the

same coordinatively unsaturated $\text{Ru}(\text{CO})_3\text{PPh}_3$ species formed by light-induced CO loss from $\text{Ru}(\text{CO})_4\text{PPh}_3$.

Loss of CO from cis-mer- $\text{HM}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ is also a primary photoreaction. Both Et_3SiH and CO can be detected upon near-UV irradiation of cis-mer- $\text{HM}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ in rigid alkane matrices at ~ 100 K. At 298 K, both the CO and the Et_3SiH have apparent consequence in light-induced exchange processes such as cis-mer- $\text{HM}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3) + \text{Ph}_3\text{SiH} \rightarrow$ cis-mer- $\text{HM}(\text{SiPh}_3)(\text{CO})_3(\text{PPh}_3) + \text{Et}_3\text{SiH}$. The CO loss can also lead to dicarbonyl photoproducts in the presence of small π -donor ligands, but such photosubstitution products have not been isolated. The intriguing possibility is that irradiation of cis-mer- $\text{HM}(\text{SiR}_3)(\text{CO})_3(\text{PPh}_3)$ in the presence of an alkene might yield $\text{HM}(\text{SiR}_3)(\text{CO})_2(\text{alkene})(\text{PPh}_3)$, possibly a precursor to the catalytic products observed when $\text{M}(\text{CO})_4\text{PPh}_3$ is irradiated in the presence of an excess of a 1/1 mole ratio of $\text{R}_3\text{SiH}/\text{alkene}$.³ At least, loss of CO as a primary result from photoexcitation of cis-mer- $\text{HM}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ provides a rationale for the observed photocatalysis of $\text{R}_3\text{SiH}/\text{alkene}$ mixtures.

Observation of light-induced reductive elimination of R_3SiH from a metal complex raises the question of the nature of the excited state responsible for such chemistry. Given the similarity in the chemistry of H-H and $\text{R}_3\text{Si-H}$ with respect to oxidative addition, it is reasonable to expect that excited states of $\text{MH}(\text{SiR}_3)$ species will be similar to those for MH_2 species.² One difference of note, however, is that the nature of $-\text{SiR}_3$ can be "tuned" by varying R. Work is underway to establish whether light-induced reductive elimination of R_3SiH is as general as H_2 elimination.

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Table I. IR and UV-VIS Spectroscopic Data for Relevant Compounds.

Compound	Medium (T, K)	IR		UV-VIS λ_{\max} , nm(ϵ)
		ν_{CO} , cm^{-1}	(ref. 0D)	
$\text{Fe}(\text{CO})_4\text{PPh}_3$	3-methylpentane (100) 2-MeTHF (100)	2052(1.8), 1979(1.0), 1946(3.3) 2046(1.6), 1966(1.0), 1938(3.2)		274, 266, 260 ^a
$\text{Fe}(\text{CO})_3\text{PPh}_3$	3-methylpentane(100)	2004(1.7), 1918(1.0), 1884(1.5)		
$\text{Fe}(\text{CO})_3(\text{PPh}_3)(2\text{-MeTHF})$	2-MeTHF (100)	1977(1.1), 1888(1.0), 1859(1.6)		
$\text{Fe}(\text{CO})_2(\text{PPh}_3)(2\text{-MeTHF})_2$	2-MeTHF (100)	1903(1.0), 1816(1.7)		
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	3-methylpentane (298)	1895		
$\text{Fe}(\text{CO})_3(\text{PPh}_3)(\text{P}(\text{OCH}_2)_3\text{CEt})$	2-MeTHF (298)	1909		
$\text{Fe}(\text{CO})_3(\text{PPh}_3)(1\text{-C}_5\text{H}_{10})$	1-C ₅ H ₁₀ (100)	2013(2.9), 1951(1.0), 1916(2.7)		
<u>cis-mer</u> -HFe(SiEt ₃)(CO) ₃ (PPh ₃)	3-methylpentane (298)	2032(1.0), 1980(6.7), 1961(16.0)		275, 260
<u>fac</u> -HFe(SiEt ₃)(CO) ₃ (PPh ₃)	Et ₃ SiH (100)	2035(1.4), 1971(1.0)		
<u>trans-mer</u> -HFe(SiEt ₃)(CO) ₃ (PPh ₃)	3-methylpentane (298)	2061(1.0), 1999(2.4)		
<u>cis-mer</u> -HFe(SiPh ₃)(CO) ₃ (PPh ₃)	2-MeTHF (298)	2040(1.0), 1985(sh), 1972(23.0)		280, 240
<u>cis-mer</u> -HFe[Si(OMe) ₃](CO) ₃ (PPh ₃)	3-methylpentane (298)	2052(1.0), 1994(sh), 1982(-20)		
<u>cis-mer</u> -HFe[Si(OEt) ₃](CO) ₃ (PPh ₃)	3-methylpentane (298)	2051(1.0), 1994(sh), 1980(-17)		

Table I. IR and UV-VIS Spectroscopic Data for Relevant Compounds.

Compound	Medium (T, K)	IR		UV-VIS	
		ν_{CO}, cm^{-1}	(rel. OD)	$\lambda_{max}, \text{nm}(\epsilon)$	
$\text{Ru}(\text{CO})_4\text{PPh}_3$	methylcyclohexane (100)	2060(2.2), 1984(1.0), 1951(3.8)		268(sh), 259(9400) ^a	
	2-MeTHF (100)	2055(1.8), 1978(1.0), 1948(3.2)			
$\text{Ru}(\text{CO})_3\text{PPh}_3$	methylcyclohexane (100)	2027(1.0), 1908(1.3)		425, 342	
$\text{Ru}(\text{CO})_3(\text{PPh}_3)(2\text{-MeTHF})$	2-MeTHF (100)	1999(1.0), 1902(1.1), 1871(1.5)			
$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$	methylcyclohexane (298)	1908			
$\text{Ru}(\text{CO})_3(\text{PPh}_3)(\text{P}(\text{OCH}_2)_3\text{Cet})$	methylcyclohexane (298)	1932			
$\text{Ru}(\text{CO})_3(\text{PPh}_3)(1\text{-C}_5\text{H}_{10})$	1-C ₅ H ₁₀ (100)	2035(1.5), 1967(1.3), 1935(1.0)		270(sh), 228(sh)	
<u>cis-mer</u> -HRu(SiEt ₃)(CO) ₃ (PPh ₃)	methylcyclohexane (298)	2066(1.0), 2009(9.0), 1992(17.5)			
<u>fac</u> -HRu(SiEt ₃)(CO) ₃ (PPh ₃)	Et ₃ SiH (100)	2065(1.0), 2003(1.1)			
<u>cis-mer</u> -HRu(SiPh ₃)(CO) ₃ (PPh ₃)	methylcyclohexane (298)	2071(1.0), 2022(3.6), 2007(9.0)			
<u>cis-mer</u> -HRu(SiMeCl ₂)(CO) ₃ (PPh ₃)	n-hexane (298)	2098(1.0), 2042(5.5), 2021(11.0)			
<u>cis-mer</u> -HRu[Si(OMe) ₃](CO) ₃ (PPh ₃)	methylcyclohexane (298)	2086(1.0), 2032(4.7), 2006(9.6)			
<u>cis-mer</u> -HRu[Si(OEt) ₃](CO) ₃ (PPh ₃)	methylcyclohexane (298)	2090(1.0), 2025(4.3), 2008(9.7)			
HRu(SiEt ₃)(CO) ₂ (PPh ₃)(P(OCH ₂) ₃ Cet)	methylcyclohexane (298)	1974			

^aTemperature for these measurements was 298 K.

Table II. NMR Data for Relevant Compounds.^a

Compound	¹ H, δ ppm ^b	¹³ C, δ ppm ^b
Fe(CO) ₄ PPh ₃ ^c	PPh ₃ , 7.38(m)	CO, 221.0 [² J _{P-C} = 19 Hz] PPh ₃ , 134
<u>cis-mer</u> -HFe(SiEt ₃)(CO) ₃ (PPh ₃)	PPh ₃ , 7.35(m,15) Si-Et ₃ , 2.50(m,15) Fe-H, -9.13(d,1) [² J _{P-H} = 25 Hz]	CO, 219.9; 219.8; 217.4 PPh ₃ , 132.6 SiCH ₂ CH ₃ , 2.5 SiCH ₂ CH ₃ , -0.4
<u>cis-mer</u> -HFe(SiPh ₃)(CO) ₃ (PPh ₃)	SiPh ₃ , 7.67(m,15) PPh ₃ , 7.32(m,15) Fe-H, -8.44(d,1) [² J _{P-H} = 25 Hz]	-----
Ru(CO) ₄ PPh ₃	PPh ₃ , 7.24(m)	CO, 211.0 [² J _{P-C} = 5 Hz] PPh ₃ , 134.5
<u>cis-mer</u> -HRu(SiEt ₃)(CO) ₃ (PPh ₃)	PPh ₃ , 7.23(m,15) SiCH ₂ CH ₃ , 1.29(t,9) SiCH ₂ CH ₃ , 1.19(q,6) Ru-H, -6.89(d,1) [² J _{P-H} = 16 Hz]	CO, 207.7; 207.6; 205.7 PPh ₃ , 133.8 SiCH ₂ CH ₃ , 2.8 SiCH ₂ CH ₃ , -0.4
<u>cis-mer</u> -HRu(SiPh ₃)(CO) ₃ (PPh ₃)	SiPh ₃ , 7.64(m,15) PPh ₃ , 7.26(m,15) Ru-H, -6.24(d,1) [² J _{P-H} = 16 Hz]	-----

^aAll data are for benzene-d₆ solutions at 298 K unless otherwise noted.

^bChemical shifts vs. Si(CH₃)₄; peak multiplicity (d ≡ doublet, t ≡ triplet, q ≡ quartet, m ≡ multiplet) and integration is given in parentheses for ¹H-NMR.

^cMeasured as cyclohexane-d₁₂ solution at 298 K.

Table III. Product Distribution of the Reaction of $\text{Ru}(\text{CO})_4\text{PPh}_3$ or 1b with Different Ratios of $\text{Ph}_3\text{SiH}/\text{P}(\text{OCH}_2)_3\text{Cet}$ and $\text{Ph}_3\text{SiH}/\text{PPh}_3$.^a

Reactant	$[\text{Ph}_3\text{SiH}]$, mM	$[\text{P}(\text{OCH}_2)_3\text{Cet}]$, mM	$\text{HRu}(\text{SiPh}_3)(\text{CO})_3(\text{PPh}_3)/\text{Ru}(\text{CO})_3(\text{PPh}_3)(\text{P}(\text{OCH}_2)_3\text{Cet})$ ^b	Product Ratio
$\text{Ru}(\text{CO})_4\text{PPh}_3$	20	20		1.4
	100	20		2.5
<u>cis-mer</u> - $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$	20	20		1.3
	100	20		2.3
<hr/>				
	$[\text{Ph}_3\text{SiH}]$, mM	$[\text{PPh}_3]$, mM	$\text{HRu}(\text{SiPh}_3)(\text{CO})_3(\text{PPh}_3)/\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$	
$\text{Ru}(\text{CO})_4\text{PPh}_3$	20	20		0.9
	100	20		2.6
<u>cis-mer</u> - $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$	20	20		0.7
	100	20		1.8

^aIrradiations were carried out at 298 K using ~1-5 mM metal carbonyl complex and excess $\text{Ph}_3\text{SiH}/\text{P-donor}$ in methylcyclohexane. Product ratios given are $\pm 10\%$.

^bThere is a band at 1974 cm^{-1} attributed to $\text{HRu}(\text{SiEt}_3)(\text{CO})_2(\text{PPh}_3)(\text{P}(\text{OCH}_2)_3\text{Cet})$, cf. text.

Figure Captions

Figure 1. IR difference spectra accompanying near-UV photolysis of $\text{Ru}(\text{CO})_4\text{PPh}_3$ at 100 K in methylcyclohexane to yield $\text{Ru}(\text{CO})_3\text{PPh}_3$ (top), in 1- C_5H_{10} to yield $\text{Ru}(\text{CO})_3(\text{PPh}_3)(1\text{-C}_5\text{H}_{10})$ (middle), and in methylcyclohexane/ Et_3SiH (1/1) to yield cis-mer and fac- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$.

Figure 2. Top: Irradiation of $\text{Fe}(\text{CO})_4\text{PPh}_3$ in 3-methylpentane at 100 K. The negative peaks at 2052, 1978 and 1944 cm^{-1} are $\text{Fe}(\text{CO})_4\text{PPh}_3$. The positive peaks at 2004, 1918, and 1884 cm^{-1} are $\text{Fe}(\text{CO})_3\text{PPh}_3$, and the peak at 2133 cm^{-1} is due to free CO. Bottom: Irradiation of $\text{Fe}(\text{CO})_4\text{PPh}_3$ in 1-pentene at 100 K. The negative peaks at 2050, 1974, and 1941 are $\text{Fe}(\text{CO})_4\text{PPh}_3$. The positive peak at 2133 cm^{-1} is due to free CO, the positive peaks at 2013, 1951 and 1916 cm^{-1} are $\text{Fe}(\text{CO})_3(1\text{-C}_5\text{H}_{10})(\text{PPh}_3)$. The peaks at 1988 and 1888 cm^{-1} are secondary photo-products.

Figure 3. Left top: IR difference spectral changes accompanying UV irradiation of $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ in a HSiEt_3 matrix at 100 K. The negative peaks at 2051 and 1943 cm^{-1} are associated with the disappearance of $\text{Fe}(\text{CO})_4\text{PPh}_3$. The positive peaks at 2035 and 1971 cm^{-1} are attributed to fac- $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ and those at 1979 and 1959 cm^{-1} are attributed to cis-mer- $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$, 1a. Left bottom: Warm-up to 298 K yields only the cis-mer- $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ isomer at 1980 and 1961 cm^{-1} . Right top: FTIR spectral changes accompanying UV irradiation of $\text{Ru}(\text{CO})_4\text{PPh}_3$ in a HSiEt_3 /methylcyclohexane matrix at 100 K. The negative peaks at 2060, 1985 and 1952 cm^{-1} are associated with the disappearance of $\text{Ru}(\text{CO})_4\text{PPh}_3$. The positive peak at 2132 cm^{-1} is attributed to free CO. Other positive peaks include 2065 and 2003 cm^{-1} attributed to fac- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$, 2008 and 1992 cm^{-1} attributed to cis-mer- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$, 1b, and 2027 and 1906 cm^{-1}

assigned to $\text{Ru}(\text{CO})_3\text{PPh}_3$. Right bottom: Warm-up to 298 K yields only the cis-mer- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ isomer at 2067, 2009 and 1992 cm^{-1} .

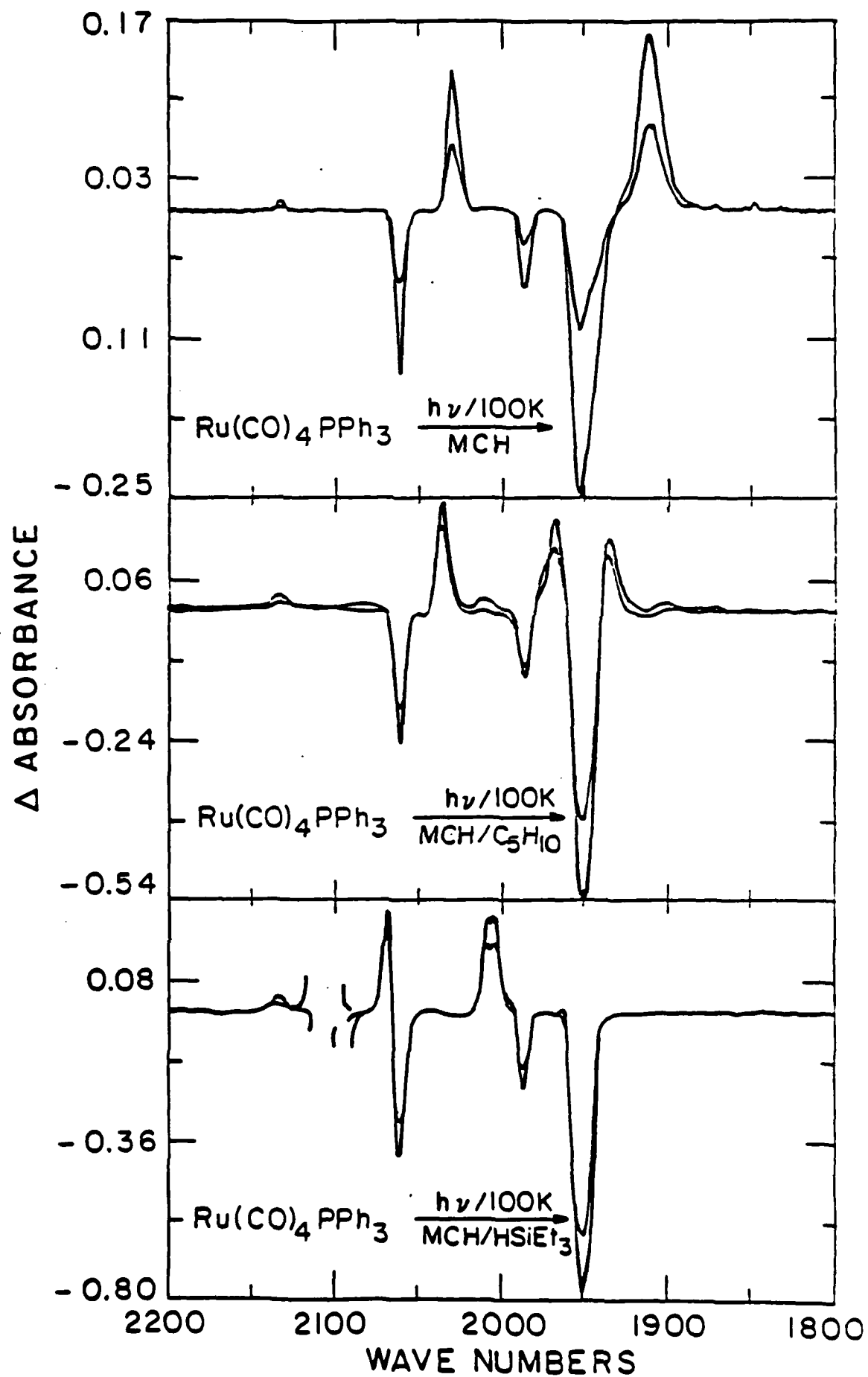
Figure 4. Top: IR difference spectral changes accompanying UV irradiation of cis-mer- $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ in a 3-methylpentane matrix at 100 K. The negative peaks at 2032, 1979 and 1960 cm^{-1} are associated with loss of cis-mer- $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. The positive peaks at 2133 and 2107 cm^{-1} are due to free CO and HSiEt_3 , respectively, while those at 2003, 1921 and 1886 cm^{-1} are attributed to the 16 valence e^- $\text{Fe}(\text{CO})_3\text{PPh}_3$. The inset shows the expansion of the free CO and HSiEt_3 region. Bottom: IR difference spectral changes accompanying UV irradiation of cis-mer- $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ in a 1:1 mixture of HSiEt_3 and 3-methylpentane at 100 K. The negative peaks are associated with the disappearance of cis-mer- $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ and the positive peaks at 2035 and 1969 cm^{-1} are attributed to fac- $\text{HFe}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. The peaks appearing at 1924 and 1895 cm^{-1} may be due to $\text{HFe}(\text{SiEt}_3)(\text{CO})_2(\text{PPh}_3)$, cf. text.

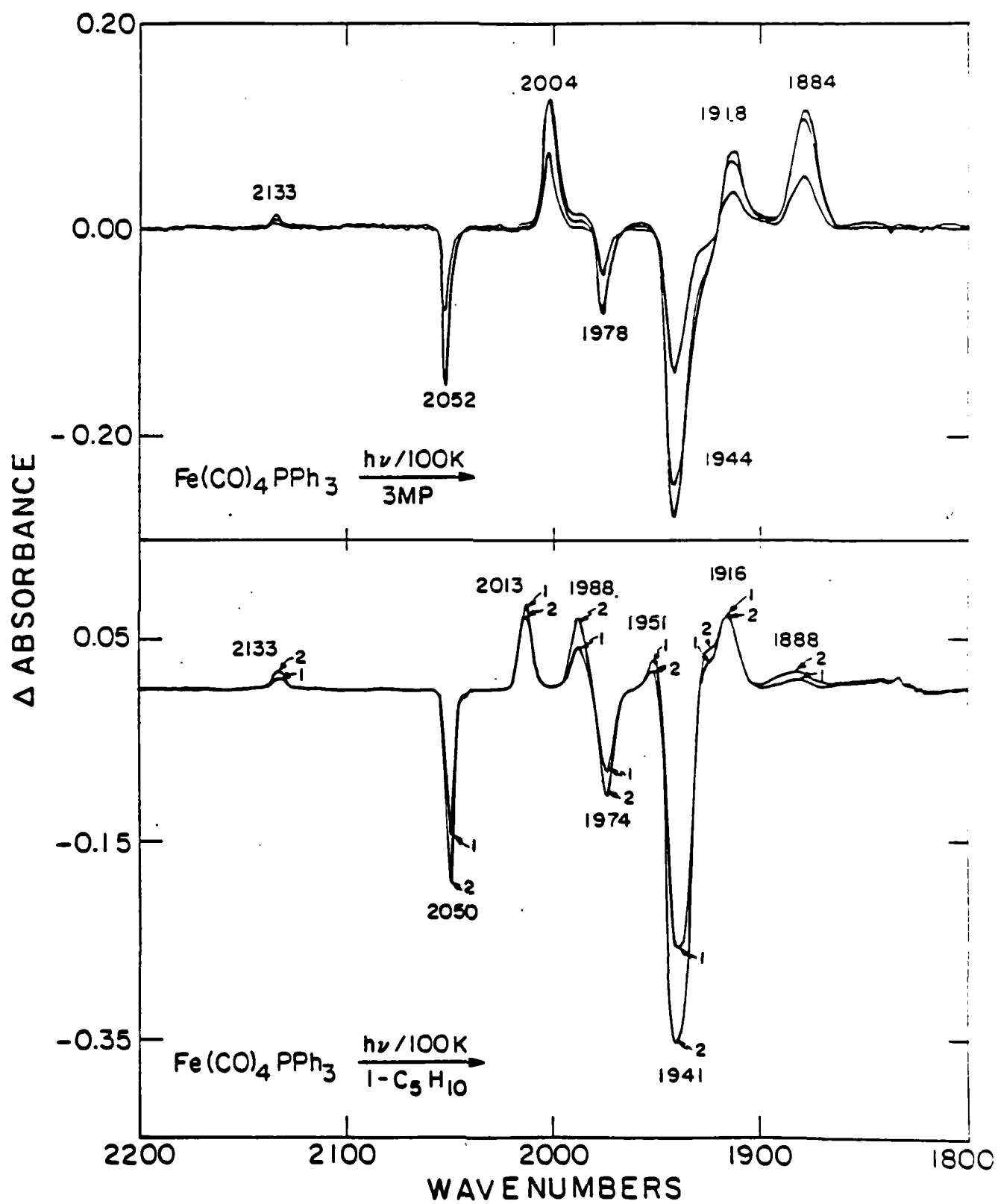
Figure 5. Top: IR difference spectral changes accompanying UV irradiation of cis-mer- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ in a methylcyclohexane matrix at 100 K. The negative peaks at 2069, 2009 and 1990 are associated with the disappearance of cis-mer- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. The positive peaks at 2132 and 2104 cm^{-1} are due to free CO and HSiEt_3 , respectively. Other positive peaks include 2066 and 2001 cm^{-1} attributed to fac- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ and 2028 and 1911 cm^{-1} attributed mainly to the 16 valence e^- $\text{Ru}(\text{CO})_3\text{PPh}_3$ of C_{3v} symmetry. The peaks at 1985 and 1947 cm^{-1} may be due to $\text{HRu}(\text{SiEt}_3)(\text{CO})_2(\text{PPh}_3)$, cf. text. Inset shows the expansion of the free CO and HSiEt_3 region. Bottom: IR difference spectral changes accompanying UV irradiation of cis-mer- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$ in a 1- C_5H_{10} matrix. The negative peaks are associated with loss of mer- $\text{HRu}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. The positive peaks at 2132 and 2101 cm^{-1} are due to free CO and HSiEt_3 ,

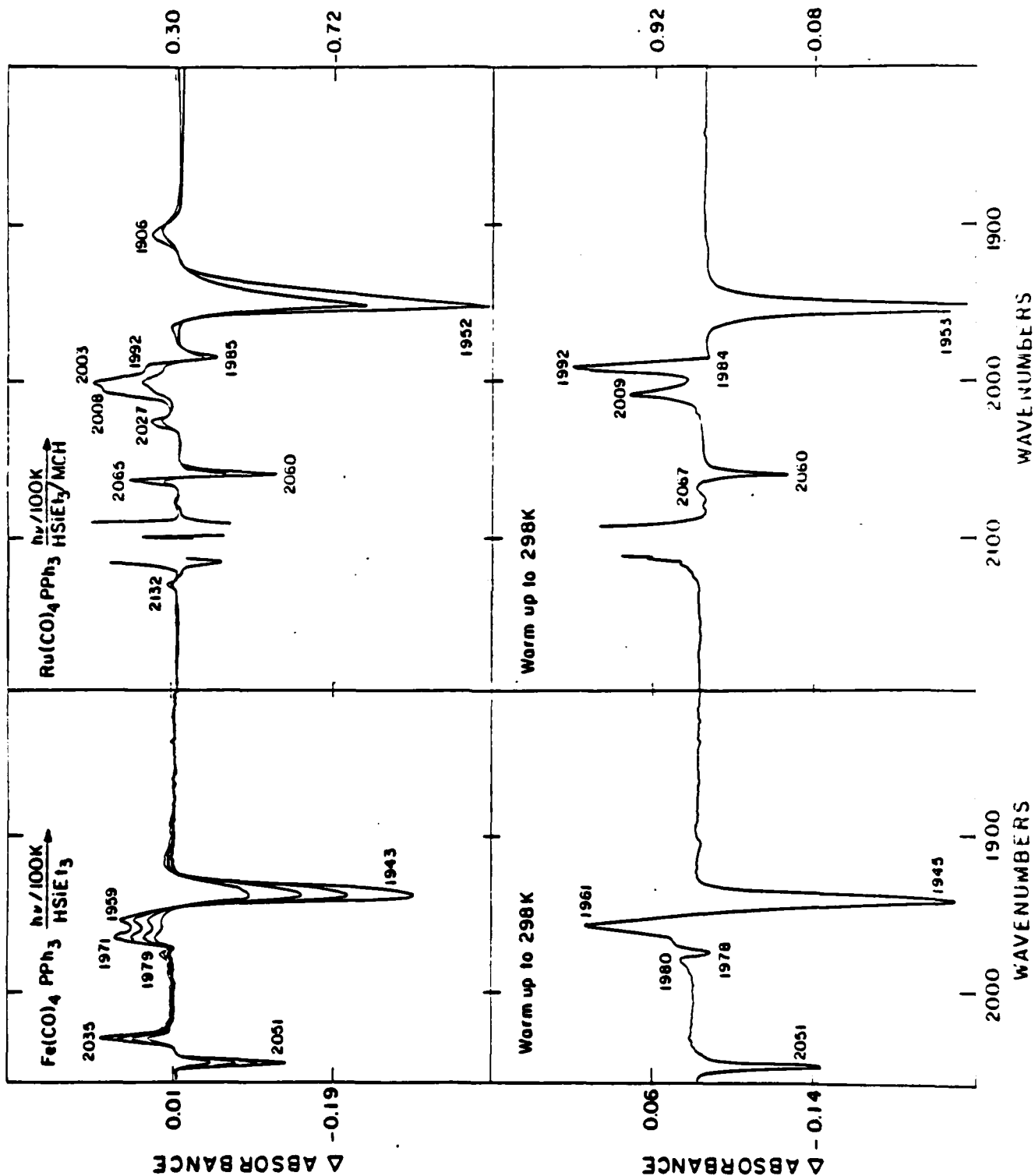
respectively. Other positive peaks include 2066 cm^{-1} attributed to fac-HRu(SiEt₃)(CO)₃(PPh₃), and 2034, 1966 and 1937 cm^{-1} attributed to Ru(CO)₃(PPh₃)₂. The peak at 1954 cm^{-1} may be due to HRu(SiEt₃)(CO)₂(1-C₅H₁₀)(PPh₃) or to secondary photolysis products, cf. text. Inset shows the expansion of the free CO and HSiEt₃ region.

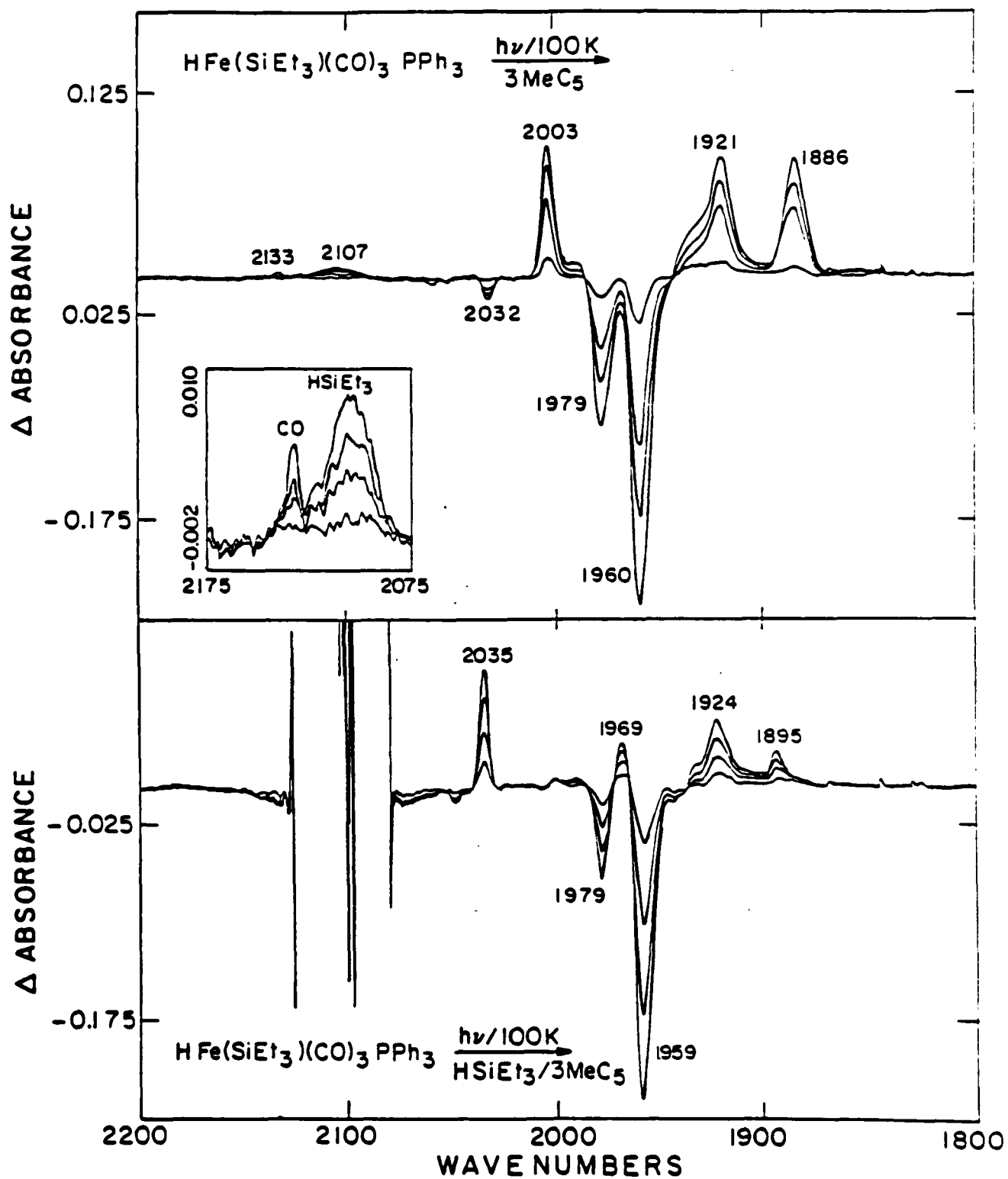
Figure 6. Left top: IR difference spectral changes upon irradiation of cis-mer-HFe(SiEt₃)(CO)₃(PPh₃) in the presence of excess PPh₃ in 3-methylpentane solution at 298 K. The negative peaks are associated with the loss of cis-mer-HFe(SiEt₃)(CO)₃(PPh₃). The positive peak at 2103 cm^{-1} is attributed to HSiEt₃ and that at 1895 cm^{-1} is due to Fe(CO)₃(PPh₃)₂. The peaks at 1844 and 1814 cm^{-1} are due to secondary photoproducts. Left bottom: IR difference spectral changes upon irradiation of cis-mer-HFe(SiPh₃)(CO)₃(PPh₃) in the presence of excess HSiEt₃ in 2-MeTHF solution at 298 K. The negative peak at 2102 cm^{-1} is due to disappearance of HSiEt₃ and those at 1987 and 1971 cm^{-1} are due to disappearance of cis-mer-HFe(SiPh₃)(CO)₃(PPh₃). The positive peak at 2130 cm^{-1} is attributed to HSiPh₃ and those at 2029 and 1957 cm^{-1} are attributed to mer-HFe(SiEt₃)(CO)₃(PPh₃). The inset shows the ¹H-NMR spectrum of cis-mer-HFe(SiPh₃)(CO)₃(PPh₃) in HSiEt₃/C₆D₆ at 298 K before and after 10 min irradiation, showing only the upfield metal-hydride region. The doublet at -8.39 and -8.49 ppm is the Fe-H resonance of cis-mer-HFe(SiPh₃)(CO)₃(PPh₃) and the new doublet at -9.08 and -9.18 ppm is attributed to the Fe-H resonance of cis-mer-HFe(SiEt₃)(CO)₃(PPh₃). Right top: IR difference spectral changes upon irradiation of cis-mer-HRu(SiEt₃)(CO)₃(PPh₃) in the presence of excess PPh₃ in methylcyclohexane solution at 298 K. The negative peaks are associated with the loss of cis-mer-HRu(SiEt₃)(CO)₃(PPh₃). The positive peak at 2101 cm^{-1} is attributed to HSiEt₃ and that at 1908 cm^{-1} is due to Ru(CO)₃(PPh₃)₂. The peaks at 1872, 1830 and 1819 cm^{-1} are due to secondary photoproducts. Right bottom: IR difference spectral changes upon irradiation of cis-mer-HRu(SiEt₃)-

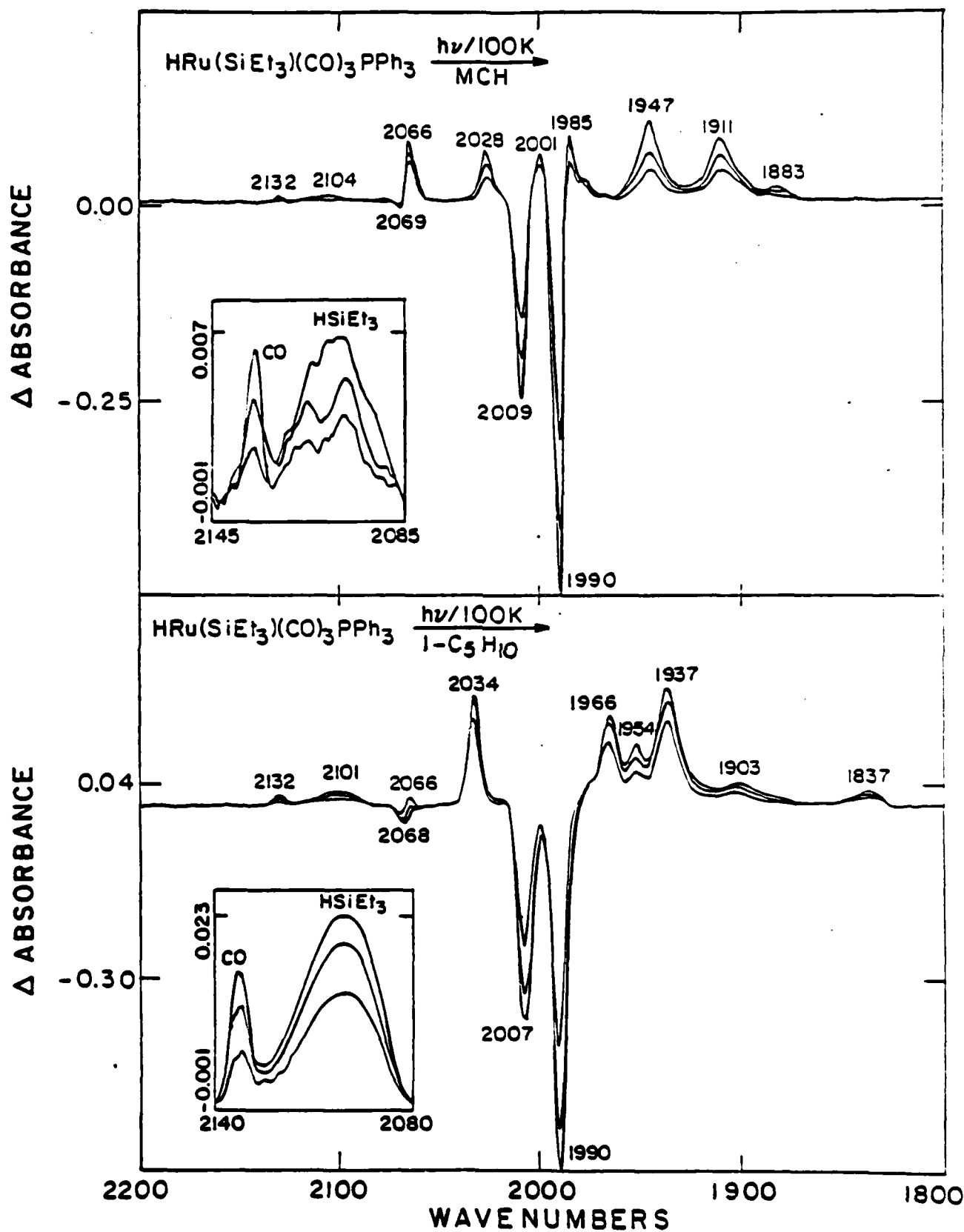
(CO)₃(PPh₃) in the presence of excess HSiPh₃ in methylcyclohexane solution at 298 K. The negative peak at 2130 cm⁻¹ is due to disappearance of HSiPh₃ and those at 2067 and 1991 cm⁻¹ are due to disappearance of cis-mer-HRu(SiEt₃)(CO)₃(PPh₃). The positive peak at 2101 cm⁻¹ is attributed to HSiEt₃ and those at 2074, 2022 and 2005 cm⁻¹ are attributed to cis-mer-HRu(SiPh₃)(CO)₃(PPh₃). The inset shows the ¹H-NMR spectrum of cis-mer-HRu(SiEt₃)(CO)₃(PPh₃) in HSiPh₃/C₆D₆ at 298 K before and after 10 min irradiation, showing only the upfield metal-hydride region. The doublet at -6.85 and -6.92 ppm is the Ru-H resonance of cis-mer-HRu(SiEt₃)(CO)₃(PPh₃), and the new doublet at -6.21 and -6.27 ppm is attributed to the Ru-H resonance of cis-mer-HRu(SiPh₃)(CO)₃(PPh₃).

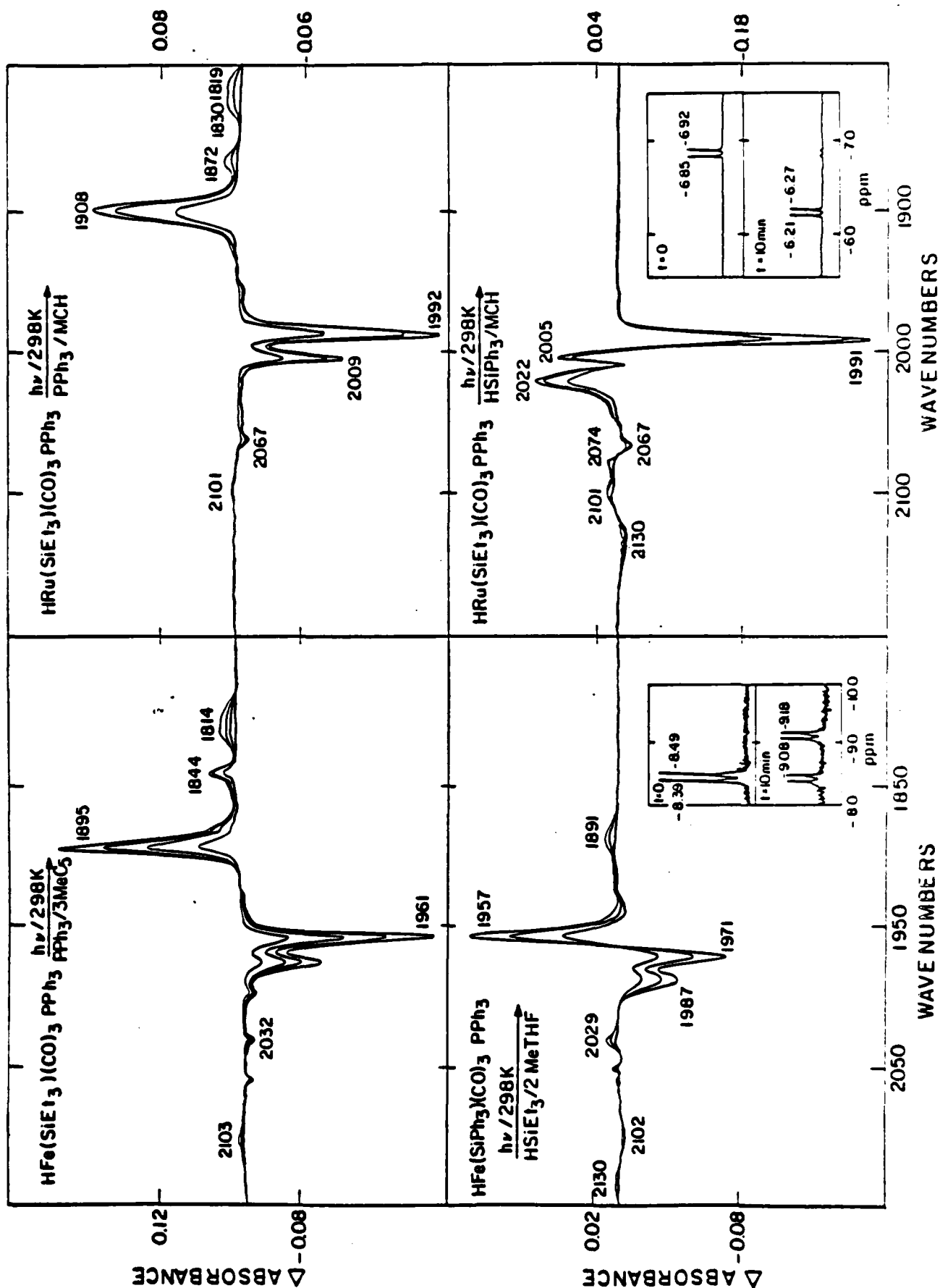












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